

Corrections to a mean number of droplets in nucleation

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Abstract

Corrections to a mean number of droplets appeared in the process of nucleation have been analyzed. The two stage model with a fixed boundary can not lead to a write result. The multi stage generalization of this model also can not give essential changes to the two stage model. The role of several first droplets have been investigated and it is shown that an account of only first droplet with further appearance in frame of the theory based on the averaged characteristics can lead to a suitable results. Both decay of metastable phase and smooth variations of external conditions have been investigated.

1 Introduction

Up to the last years a kinetic descriptions of nucleation processes were based on the averaged intensity of droplets appearance, i.e. on the rate of nucleation. Namely the rate of nucleation is considered as a central characteristic of the first order phase transition. But the supercritical droplets appear in the system occasionally and this feature has to be taken into account. Since [6], [5], [7] several attempts to include stochastic effects of droplets appearance were made. Unfortunately, they could not give an adequate and rather precise description of stochastic effects.

The arguments in justification of kinetics based on the averaged characteristics (see [4]) remain valid even after stochastic formulation of the nucleation problem has been presented. When the number of droplets in the system is very big the result of the theory based on the averaged characteristics (TAC)

is precise. Namely the number of droplets is the central characteristic of the nucleation process and it is calculated in experiments. When the number of droplets appeared in a system isn't so great (in the free molecular regime of growth it occurs only due to a volume of a system) one can speak about corrections to a mean value of the total number of droplets appeared in the system in comparison with result predicted by TAC. This value will be the main object of investigation here.

In diffusion regime of the droplets growth the kinetic description is based on special models (see [1]) and there is no need to analyze this regime here. So, in this paper only the free molecular regime of droplets growth will be considered.

In investigation of stochastic effects of nucleation one can see rather easy that the first correction terms are equal to zero. So, there appear a problem to calculate the higher terms of decomposition. It is rather difficult to perform precise calculations and we shall be interested at least to get estimates for these coefficients to prove the smallness of the total amount of corrections. But even the calculation of the very first terms meets technical difficulties (see [7], [5]). One has also to stress that the zero shift found in these papers was a natural result of linearization made to overcome technical difficulties. Then it can not be considered there as a true physical result, but only the consequence of linearization. So, it is necessary to propose a method to calculate the estimates for coefficients in asymptotic expansions due to stochastic corrections of nucleation.

There are two characteristic situations of external conditions in which kinetics of nucleation ordinary was constructed. These conditions are:

- decay of metastable phase when at some moment the metastable phase is created and later there is no external influence on the system;
- smooth variation of external influence on the system.

In both situations corrections will be established.

The structure of the further analysis is following:

- At first we shall analyze the two stage model with a fixed boundary. The result will be disappointing - one can not reproduce the results of numerical simulation. This corresponds to the difficulties of this model in prediction of the value of dispersion.

- To improve results we shall use the multi stage generalization of the last model. But corrections to the two stage model will be small and this can not lead to suitable results.
- Then a new approach will be used. We shall analyze the role of stochastic appearance of the first droplets. Results will be very fruitful and one can see that already account of one droplet will lead to success.
- All these considerations will be made both for decay of metastable phase and for the smooth variations of external conditions.

2 Decay of metastable phase

The kinetics of nucleation in frames of the theory based on averaged characteristics (TAC) can be described by the following equation

$$g(z) = \int_0^z (z-x)^3 \exp(-g(x)) dx$$

where unknown function g is the renormalized value of the number of molecules in a liquid (new) phase. This result can be found in [8]. The meaning of variables z, x can be also found in [8]. Since [8] it is known that one can describe kinetics in frames of monodisperse approximation, i.e.

$$g(z) = N_{eff}(z) z^3$$

where N_{eff} is the effective number of droplets in monodisperse peak, namely

$$N_{eff}(z) = z/4$$

The monodisperse approximation can be chosen as the fixed (not floating) monodisperse approximation (see [8]) and leads to the following expression for the size spectrum

$$f(x) = f_* \exp(-N_{eff} x^3)$$

Here f_* is the amplitude of spectrum,

$$N_{eff} = N(\Delta x/4)$$

and Δx is a width of a whole spectrum (connected with the duration of a nucleation period).

The total number of droplets can be obtained on the base of f as

$$N_{tot} = \int_0^\infty dx f(x)$$

For N_{eff} we have a Gaussian distribution with standard dispersion since formation of the first N_{eff} droplets can be treated as the sequence of independent events

$$P(N_{eff}) \sim \exp\left(-\frac{(N_{eff} - \langle N_{eff} \rangle)^2}{2 \langle N_{eff} \rangle}\right)$$

Here $\langle N_{eff} \rangle$ is the mean value of N_{eff}

Then for the averaged value of N_{tot} , i.e. for $\langle N_{tot} \rangle$ we have the following formula

$$\langle N_{tot} \rangle = \int_{-\infty}^{\infty} dN_{eff} P(N_{eff}) f_* \int_0^\infty \exp(-N_{eff} x^3) dx$$

Now with the help of formula

$$\int dy \exp(-ya) \exp(-c(y-b)^2) \sim \exp(-ba + \frac{a^2}{4c})$$

we fulfill integration over N_{eff} . Here $b = \langle N_{eff} \rangle$, $a = x^3$, $c^{-1} = 2 \langle N_{eff} \rangle$. As the result we have

$$\langle N_{tot} \rangle \sim \int_0^\infty \exp(-\langle N_{eff} \rangle x^3 + \frac{x^6}{2 \langle N_{eff} \rangle}) dx \quad (1)$$

The second term in exponent, i.e. $\frac{x^6}{2 \langle N_{eff} \rangle}$ is the correction term which can be seen from

$$\langle N_{tot} \rangle \sim f_*^{3/4} \int_0^\infty \exp(-y^3 + \frac{y^6}{2 \langle N_{eff} \rangle}) dy$$

As a rough estimate we can take y in correction term as $y \approx 1$ and get

$$\langle N_{tot} \rangle = \langle N_{tot\ 0} \rangle \exp\left(\frac{1}{2 \langle N_{eff} \rangle}\right)$$

where $\langle N_{tot\ 0} \rangle$ is the value N_{tot} calculated without stochastic effects taken into account, i.e. in frames of TAC. Then for this value one can get expression

$$\langle N_{tot\ 0} \rangle \sim \int_0^\infty \exp(-\langle N_{eff} \rangle x^3) dx$$

Having noticed that

$$\langle N_{eff} \rangle \approx \langle N_{tot\ 0} \rangle / 4$$

we get

$$\langle N_{tot} \rangle = \langle N_{tot\ 0} \rangle \exp\left(\frac{2}{\langle N_{eff} \rangle}\right)$$

Decomposition of exponent gives

$$\langle N_{tot} \rangle = \langle N_{tot\ 0} \rangle + 2 + \frac{2}{\langle N_{tot\ 0} \rangle} + \dots$$

Another more balanced variant of consideration is to use decomposition of

$$\exp\left(\frac{x^6}{2} \langle N_{eff} \rangle\right) = 1 + \frac{x^6}{2} \langle N_{eff} \rangle + \frac{x^{12}}{8} \langle N_{eff} \rangle^2$$

already in (1). At least the integral then will have no problems with convergence. We have

$$\langle N_{tot} \rangle \sim \int_0^\infty \exp(-\langle N_{eff} \rangle x^3) \left(1 + \frac{x^6}{2} \langle N_{eff} \rangle + \frac{x^{12}}{8} \langle N_{eff} \rangle^2\right) dx$$

Integration can be fulfilled separately for every term in decomposition. Then we come to

$$\langle N_{tot} \rangle = \langle N_{tot\ 0} \rangle + A_1 + \frac{A_2}{\langle N_{tot\ 0} \rangle} + \dots$$

where constants A_1 and A_2 are given by

$$A_1 = 2 \int_0^\infty \exp(-y^3) y^6 dy / \int_0^\infty \exp(-y^3) dy = 8/9$$

$$A_2 = 2 \int_0^\infty \exp(-y^3) y^{12} dy / \int_0^\infty \exp(-y^3) dy = 510/89 = 6.91$$

From the functional forms of expressions for A_i one can see that A_1 is determined rather smart while the error in A_2 can be essential. The reason is the rapidly growing term y^{12} in subintegral function. Already y^6 in expression for A_1 grows too rapidly. So, in subintegral functions the main role belong to y corresponding to droplets appeared at the very end of the nucleation period. But the form of spectrum $\sim \exp(-y^3)$ is determined at the back side of spectrum (i.e. at $y > 1$) with a low accuracy. In TAC the weight of such droplets was negligible and the result was accurate. Here the error can be

essential. That's why it is reasonable to restrict the decomposition only by the first term A_1 .

In Figure 1 one can see the results of numerical simulation (oscillating curve) and analytical approximation (smooth monotonuous curve) for the relative value

$$P = \langle N_{tot} \rangle / \langle N_{tot\ 0} \rangle - 1$$

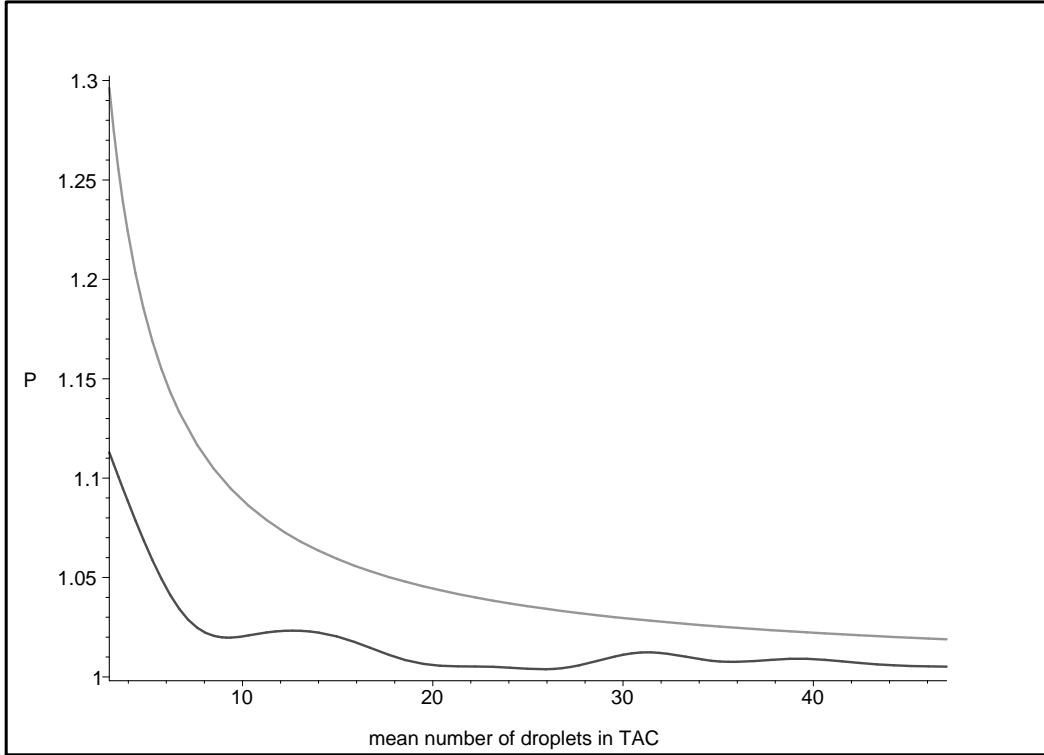


Figure 1: Numerical and analytical solutions in the situation of decay. The initial monodisperse approximation is considered.

One can see that there is no satisfactory coincidence between the theoretical result and the result of simulation. The reason is the roughness of monodisperse approximation used in [8] and applied here.

Now we shall take a more refined approximation used to calculate the value of dispersion initiated by stochastic appearance of droplets in the process of decay [9]. This approximation is the following: the length of formation of monodisperse spectrum is $2 * l$ where $l = 0.2$; the monodisperse spectrum

is formed at $2 * l - b$ where $b = 0.336$. The derivation of this approximation can be found in [9]. Here

$$\langle N_{tot\ 0} \rangle = 2l - b + \int_0^\infty \exp(-2lx^3) dx$$

Then one has to reconsider the value of A_1 . It can be done only rather approximately. One can see that A_1 is reciprocal to the total number of droplets in monodisperse spectrum which is now $2 * l = 0.4$ instead of 0.25 in initial monodisperse approximation. Then instead of previous A_1 one has to take

$$A_1 \rightarrow A_1 0.25 / 0.4 = 1/3.6$$

The results are shown in Figure 2

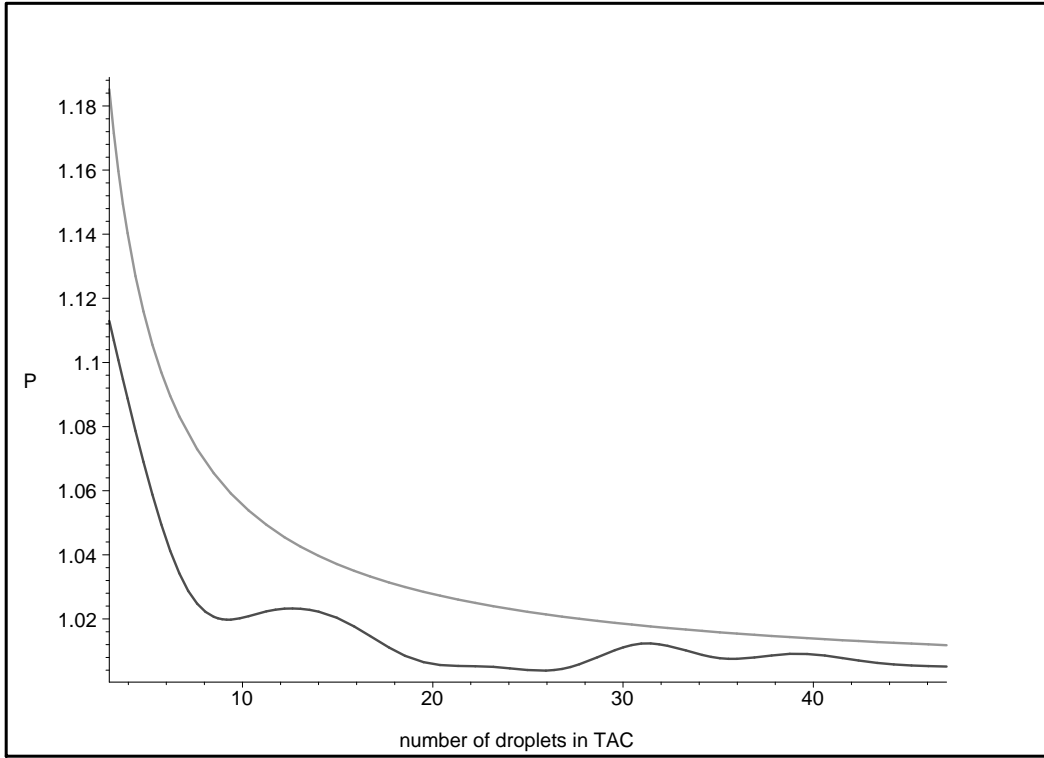


Figure 2: Numerical and analytical solutions in the situation of decay. The shifted monodisperse approximation is considered.

Here the coincidence between curves became better but it is not still satisfactory. This means that the model with a fixed boundary can not give

a good result. This corresponds to the difficulties in calculation of dispersion on the base of the model with a fixed boundary [11].

3 Smooth variations of external conditions

In the situation of smooth variation of external conditions (so called dynamic conditions) we can fulfill the same procedure.

The evolution equation in TAC looks like

$$g = c^{-1} \int_{-\infty}^{\infty} (z - x)^3 \psi(x) \exp(-g(x)) dx$$

where $\psi = \exp(x)$ describes the change of external conditions and the renormalization to cancel the coefficient in ψ is used. As a compensation for such renormalization the coefficient $c = 0.189$ or $c = 1/6$ (it depends on the type of choice of the base of decompositions (see [4])) appears.

Here we shall use the monodisperse approximation also. The monodisperse approximation was proposed in [10] where all details can be found. In the fixed monodisperse approximation one can write

$$f = f_* \exp(x - \langle N_{eff} \rangle (x + 3)^3)$$

for the spectrum of droplets sizes. Here the effective number of droplets is given by

$$N_{eff} = \frac{6c}{27}, \quad c = 0.189$$

or

$$N_{eff} = \frac{1}{27}$$

For the total number of droplets we have an evident expression

$$N_{tot} = f_* \int_{-\infty}^{\infty} dx \exp(x - \langle N_{eff} \rangle (x + 3)^3)$$

For the mean total number of droplets one can get

$$\langle N_{tot} \rangle = f_* \int dN_{eff} \int_{-\infty}^{\infty} dx \exp(x - \langle N_{eff} \rangle (x + 3)^3) P(N_{eff})$$

where $P(N_{eff})$ is the distribution function for the quantity of effective droplets.

For $P(N_{eff})$ we have an evident Gaussian distribution with dispersion of ideal gas

$$P(N_{eff}) \sim \exp\left(-\frac{(N_{eff} - \langle N_{eff} \rangle)^2}{2 \langle N_{eff} \rangle}\right)$$

Having fulfilled integration one gets

$$\langle N_{tot} \rangle \sim f_* \int_{-\infty}^{\infty} dx \exp(x - \langle N_{eff} \rangle (x+3)^3) \exp\left(\frac{(x+3)^6}{2} \langle N_{eff} \rangle\right)$$

Certainly, the last integral doesn't converge. We need a regularization which will be done below.

Then one has to decompose

$$\exp\left(\frac{(x+3)^6}{2} \langle N_{eff} \rangle\right) = 1 + \frac{(x+3)^6}{2} \langle N_{eff} \rangle + \frac{(x+3)^{12}}{8} \langle N_{eff} \rangle^2 + \dots$$

and then one can fulfill integration for every term. Now the integral has no problems with convergence.

In above formulas $\langle N_{eff} \rangle = 1/27$ which is a natural requirement to use the monodisperse approximation. To calculate correction terms one has to include explicitly the volume of the system V (i.e. the real mean number of droplets). Now we shall give the explicit formulas for correction terms. We have to calculate the value

$$\langle N_{tot} \rangle = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} \exp\left(x - \frac{N_{eff}}{V} (x+3)^3\right) \exp\left(-\frac{(N_{eff} - \tilde{N}_{eff})^2}{2\tilde{N}_{eff}}\right) dN_{eff}$$

$$\tilde{N}_{eff} \equiv \langle N_{eff} \rangle$$

Earlier we decomposed $\exp\left(-\frac{(N_{eff} - \tilde{N}_{eff})^2}{2\tilde{N}_{eff}}\right)$ and had some problems with convergence. Now we shall decompose $\exp\left(x - \frac{N_{eff}}{V} (x+3)^3\right)$. At first we shall present this exponent as

$$\exp\left(x - \frac{N_{eff}}{V} (x+3)^3\right) = \exp\left(x - \frac{\tilde{N}_{eff}}{V} (x+3)^3\right) \exp\left(-\left(\frac{N_{eff}}{V} - \frac{\tilde{N}_{eff}}{V}\right)(x+3)^3\right)$$

The decomposition of the last exponent gives

$$\exp\left(-\left(\frac{N_{eff}}{V} - \frac{\tilde{N}_{eff}}{V}\right)(x+3)^3\right) = 1 + (x+3)^3 \frac{N_{eff} - \tilde{N}_{eff}}{V} + \frac{(x+3)^6}{2} \frac{(N_{eff} - \tilde{N}_{eff})^2}{V^2} +$$

$$\frac{(x+3)^9}{6} \frac{(N_{eff} - \tilde{N}_{eff})^3}{V^3} + \frac{(x+3)^{12}}{24} \frac{(N_{eff} - \tilde{N}_{eff})^4}{V^4}$$

The calculation of integrals gives

$$\int_{-\infty}^{\infty} \exp\left(-\frac{(N_{eff} - \tilde{N}_{eff})^2}{2\tilde{N}_{eff}}\right) dN_{eff} = \sqrt{\pi}(2\tilde{N}_{eff})^{1/2}$$

$$\int_{-\infty}^{\infty} \exp\left(-\frac{(N_{eff} - \tilde{N}_{eff})^2}{2\tilde{N}_{eff}}\right) (N_{eff} - \tilde{N}_{eff})^2 dN_{eff} = \frac{1}{2} \sqrt{\pi} (2\tilde{N}_{eff})^{3/2}$$

$$\int_{-\infty}^{\infty} \exp\left(-\frac{(N_{eff} - \tilde{N}_{eff})^2}{2\tilde{N}_{eff}}\right) (N_{eff} - \tilde{N}_{eff})^4 dN_{eff} = \frac{3}{4} \sqrt{\pi} (2\tilde{N}_{eff})^{5/2}$$

We have to notice that $N_{eff} = V/27$. Then we have the decomposition

$$\begin{aligned} \langle N_{tot} \rangle = \langle N_{tot}(V = \infty) \rangle &> \left(1 + \frac{1}{2V^2} \tilde{N}_{eff} \frac{\int_{-\infty}^{\infty} \exp(x - \frac{1}{27}(x+3)^3)(x+3)^6 dx}{\int_{-\infty}^{\infty} \exp(x - \frac{1}{27}(x+3)^3) dx} \right. \\ &\quad \left. + \frac{1}{8V^4} \tilde{N}_{eff}^2 \frac{\int_{-\infty}^{\infty} \exp(x - \frac{1}{27}(x+3)^3)(x+3)^{12} dx}{\int_{-\infty}^{\infty} \exp(x - \frac{1}{27}(x+3)^3) dx} \right) \end{aligned}$$

Now we have to note that the lower limit of integrations has to be put $x = -3$ because the monodisperse approximation begins to work only at $x > -3$. The region $x < 3$ has negligible influence in the total amount of droplets. Then

$$\begin{aligned} \langle N_{tot} \rangle = \langle N_{tot}(V = \infty) \rangle &> \left(1 + \frac{1}{2V^2} \frac{2\tilde{N}_{eff}}{2} \frac{\int_{-3}^{\infty} \exp(x - \frac{1}{27}(x+3)^3)(x+3)^6 dx}{\int_{-3}^{\infty} \exp(x - \frac{1}{27}(x+3)^3) dx} \right. \\ &\quad \left. + \frac{3}{24V^4} \tilde{N}_{eff}^2 \frac{\int_{-3}^{\infty} \exp(x - \frac{1}{27}(x+3)^3)(x+3)^{12} dx}{\int_{-3}^{\infty} \exp(x - \frac{1}{27}(x+3)^3) dx} \right) \end{aligned}$$

Here there were no problems with convergence. We can calculate the integrals numerically which gives

$$\begin{aligned} \langle N_{tot} \rangle = \langle N_{tot}(V = \infty) \rangle &> \left(1 + \frac{A_1}{\langle N_{tot}(V = \infty) \rangle} + \frac{A_2}{\langle N_{tot}(V = \infty) \rangle^2} + \dots \right. \\ A_1 &= \frac{1}{2 * 27^2} \frac{\int_{-\infty}^{\infty} \exp(x - \frac{1}{17}(x+3)^3)(x+3)^6 dx}{\int_{-\infty}^{\infty} \exp(x - \frac{1}{17}(x+3)^3) dx} = 1.7 \end{aligned}$$

$$A_2 = \frac{1}{8 * 27^4} \frac{\int_{-\infty}^{\infty} \exp(x - \frac{1}{17}(x+3)^3)(x+3)^{12} dx}{\int_{-\infty}^{\infty} \exp(x - \frac{1}{17}(x+3)^3) dx} = 8.1$$

This is the final result.

Again one has to note that A_2 is determined with uncertainty caused by approximate description of the back side of spectrum. Here A_2 is calculated to see that there is no singularities in decomposition. Again it is reasonable to take into account only the first correction term.

In the situation of the smooth behaviour of external conditions there is no moment of start. The point of formation of monodisperse spectrum is $z = -3$ and it is determined in the internal point. So, when we observe the subintegral function it has a maximum not in the boundary point (as in decay when it is $z = 0$) but in an internal point near $z = -3$. The subintegral function $(z - x)^3 \psi(x) \exp(-g(x))$ is rather symmetric around $x = -3$ (in decay one can not imagine that the subintegral function is symmetric around the boundary point).

Numerical simulation and analytical result can be seen in Figure 3.

One can not see the satisfactory coincidence between theoretical result (monotonuous curve) and numerical simulation (oscillating curve). So, the used model can not give the good results.

To the data of numerical simulation one can suggest a phenomenological approximation

$$N \sim V(1 + \frac{A}{V} + \dots)$$

$$A = 5/6$$

One can establish the universality also in stochastic formulation of the problem. Then the parameter A is no more than a universal constant. The numerical simulation gives $A = 5/6$. Generally speaking one can stop here all investigations.

So, the model with a fixed boundary failed in determination of corrections to the number of droplets. One has to turn to the models with floating boundary which was successfully applied in [9], [12] to the calculation of dispersion. But in the models with a floating boundary the correction to the mean number of droplets is zero. This isn't the error of the model but the level of description is limited here.

The next step in consideration is to analyze whether one can reconsider the previous results. The fact is that in nucleation one can see some balanc-

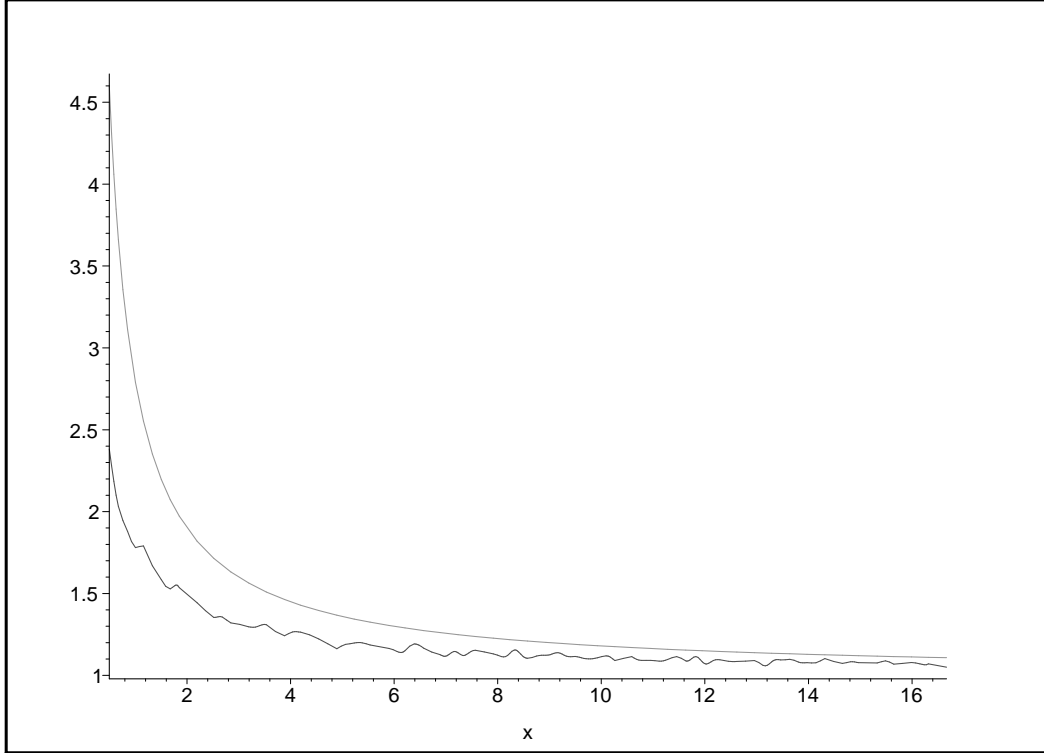


Figure 3: Numerical simulation and analytical solution under the smooth external conditions. The dependence of P over the volume of the system $V \equiv x$ is plotted.

ing forces. This can require the addition more detailed analysis containing several stages model instead of two stages.

4 Three stage scheme

In nucleation under the smooth behavior of external conditions one can observe the specific property of compensation which can damage the previous consideration. One can analytically observe the fact of compensation briefly described below which means that one can not use two stage scheme to get corrections for the mean number of droplets. The result of the three cycle scheme can be the leading term in the shift of the mean droplet number. So, we have to use the three stage scheme.

The effect of compensation in the two stage scheme require to give estimates in a three stage scheme. At first we shall explain the cancellation of effects in the two stage scheme.

The number of droplets N_{tot} can be in TAC in the monodisperce approximation calculated as

$$N_{tot}^{mean} = \int_{-3}^{\infty} \exp(x - N_{eff}(x + 3)^3) dx$$

Here N_{eff} is $1/27$.

If due to stochastic effects the necessary number N_{eff} appeared up to the "moment" $z = -3 - \delta$ instead of $z = -3$ then we have to calculate N_{tot} as

$$N_{tot}(\delta) = \int_{-3-\delta}^{\infty} \exp(x - N_{eff}(x + 3 + \delta)^3) dx$$

The calculation gives

$$N_{tot}(\delta) = \int_{-3}^{\infty} \exp(-\delta) \exp(y - N_{eff}(y + 3 + \delta)^3) dy$$

for $y = x + \delta$ and

$$N_{tot}(\delta) = \langle N_{tot} \rangle \exp(-\delta)$$

Now we shall establish the distribution $P(\delta)$ of the shift δ . The distribution $P(N_{eff})$ is the ordinary Gaussian distribution

$$P(N_{eff}) \sim \exp\left(-\frac{(N_{eff} - 1/27)^2}{2/27}\right)$$

To get $P(\delta)$ we use

$$P(N_{eff}) dN_{eff} = P(\delta) d\delta$$

The derivative $dN_{eff}/d\delta$ is

$$\frac{dN_{eff}}{d\delta} = \exp(\delta)$$

Then

$$P(\delta) = P(N_{eff}) \exp(\delta)$$

The second factor completely compensates the shift in the total number of droplets. Really,

$$\langle N_{tot} \rangle = \int P(\delta) N_{tot}(\delta) d\delta = N_{tot}^{mean}$$

This compensation shows the zero effect in the shift of droplets number in the two cycle scheme and requires to consider the three stage scheme.

Consider the three stage scheme qualitatively. We have to mention that the value N_{eff} doesn't purely appear under the ideal conditions. Already at $z = -3$ the small part of substance is in the droplets. The main consumers of vapor at $z = -3$ are the droplets appeared at $z = -6$. Here we can use also the modisperce approximation and present g at $z = -3$ as

$$g(z = -3) = N_{init}(z + 6)^3$$

with parameter N_{init} of initial monodisperce approximation.

Since the stochastic number \hat{N}_{init} doesn't coincide with the value \bar{N}_{init} calculated in TAC we can see the deviation of stochastic value $\hat{g}(z = -3)$ from the value $\bar{g}(z = -3)$ calculated in TAC.

It seems that we come to the situation which has been already described in the two stage scheme. But now we don't observe the effect of compensation because this effect takes place only due to the integration in the infinite limits. But here such an integration is absent - moreover we need the effect up to the fixed moment $z = -3$. So, we shall see the effect which results in the difference of the mean value $\langle g(z = -3) \rangle$ from $\bar{g}(z = -3)$. Then we see the regular shift δz of the moment until which the number of droplets N_0 appears. This regular shift leads to the regular shift in the total number of droplets.

Now we fulfill the computations. The number of droplets formed until $z_l = -3$ in TAC is

$$\bar{N}_{eff} = \int_{-\infty}^{-3} \exp(x - k\bar{N}_{init}(x + 6)^3) dx$$

Parameter k has here a role like c^{-1} in the two cycle scheme had.

The distribution $P(\hat{N}_{init})$ of the stochastic number of initial droplets \hat{N}_{init} has a normal Gaussian form

$$P(\hat{N}_{init}) \sim \exp\left(-\frac{(\hat{N}_{init} - \bar{N}_{init})^2}{2\bar{N}_{init}}\right)$$

The value of dispersion here corresponds to the fact that we have a free stochastic appearing of droplets.

Here appeared a special question whether it is possible to write the gaussian distribution for the total number of events (here it is the number of appeared droplets). But this question can solved positively.

Then

$$\langle \hat{N}_{eff}(z = -3) \rangle = \int P(\hat{N}_{init}) \exp(x - k\hat{N}_{init}(x + 6)^3) dx$$

Hence

$$\langle \hat{N}_{eff}(z = -3) \rangle \neq \bar{N}_{eff}$$

Then we can calculate the regular shift δz along z -axis for the moment until \bar{N}_{eff} droplets appeared. For the value of δz we get

$$\delta z = \frac{\exp(-3) \frac{\bar{N}_{eff} - \langle \hat{N}_{eff} \rangle}{\bar{N}_{eff}}}{\exp(x|_{x=-3} - k\bar{N}_{init}(x|_{x=-3} + 6)^3)}$$

Denote by δ the following value

$$\delta = \hat{N}_{init} - \bar{N}_{init}$$

Let us calculate $\langle \hat{N}_{eff} \rangle$

$$\langle \hat{N}_{eff}(z = -3) \rangle = \int_{-\infty}^{\infty} d\delta \int_{-\infty}^{-3} dx \frac{\exp(-\delta^2 2\bar{N}_{init}V^{-1})}{\sqrt{2\pi\bar{N}_{init}V^{-1}}} \exp(x - k(\bar{N}_{init} + \delta)(x + 6)^3) V$$

Recall that V is the volume of the system and here we have to introduce it explicitly.

We fulfill the calculations and get

$$\langle \hat{N}_{eff}(z = -3) \rangle = \int_{-\infty}^{\infty} d\delta \int_{-\infty}^{-3} dx \frac{\exp(-\delta^2 2\bar{N}_{init}V^{-1})}{\sqrt{2\pi\bar{N}_{init}V^{-1}}} \exp(x - k\bar{N}_{init}(x + 6)^3) V (1 - k\delta(x + 6)^3 + \frac{k}{2}\delta^2(x + 6)^6)$$

Then the deviation between $\langle \hat{N}_{eff}(z = -3) \rangle$ and $\langle \bar{N}_{eff}(z = -3) \rangle$ will be

$$\begin{aligned} & \langle \hat{N}_{eff}(z = -3) \rangle - \langle \bar{N}_{eff}(z = -3) \rangle = \\ & \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} dy \int_{-\infty}^{-3} dx \exp(-y^2) \exp(x - k\bar{N}_{init}(x + 6)^3) \frac{k^2}{2} y^2 (x + 6)^6 (2\bar{N}_{init}V)^{-1} \end{aligned}$$

Since the monodisperse approximation becomes suitable only at $z = -6$ it is more reasonable to write

$$\langle \hat{N}_{eff}(z = -3) \rangle - \langle \bar{N}_{eff}(z = -3) \rangle =$$

$$\frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} dy \int_{-6}^{-3} dx \exp(-y^2) \exp(x - k\bar{N}_{init}(x+6)^3) \frac{k^2}{2} y^2 (x+6)^6 \bar{N}_{init} V^{-1}$$

Then for the average number of droplets appeared in the system

$$\langle \hat{N}_{eff}(z = -3) \rangle V = (\bar{N}_{eff}(z = -3)|_{\bar{N}_{eff}(z=-3)=\exp(-3)} + C_0 V^{-1}) V$$

where

$$C_0 = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} dy \int_{-6}^{-3} dx \exp(-y^2) \exp(x - k\bar{N}_{init}(x+6)^3) \frac{k^2}{2} y^2 (x+6)^6 \bar{N}_{init}$$

Here we use $\bar{N}_{eff}(z = -3) = \exp(-3)$ for the number of droplets in the unit of the system because namely this value corresponds to the characteristic unperturbed value of droplets and the choice

$$\bar{N}_{init} = \exp(-6)$$

which was used in the last formula.

The numerical calculations gives the value of shift δz

$$\delta z = \frac{C_0}{\exp(-3)V} \approx \frac{0.01}{V}$$

The shift in the total number of droplets can be easily calculated since

$$\langle N_{tot} \rangle = \exp(\delta z) \bar{N}_{tot}$$

Hence

$$\langle N_{tot} \rangle \approx \bar{N}_{tot} \left(1 + \frac{w}{V}\right)$$

$$w \sim 0.01$$

Quite analogously one can show the smallness of corrections in a three cycle scheme in the situation of decay.

The result of performed calculations shows the smallness of corrections to the mean value of the total number of droplets appeared in the processes of nucleation under the conditions of decay and under the smooth behavior of external conditions.

Correction terms calculated by the theoretical derivations in the three cycle scheme are so small that they can not be confirmed both by numerical simulations and experimental researches. So, generally speaking one has to

say that these stochastic corrections don't appear in any practically significant terms of decompositions.

This result shows that there is no sense to fulfill the procedure of renormalization analogous to that used in [11] in calculation of dispersion in terms of two cycle explicit model with a fixed boundary.

Estimating the total result we have to stress that the weak feature of the presented method is the approximate knowledge of the back side of the size spectrum $\exp(-x^3)$ in decay and $\exp(x - (x+3)^3/3^3)$ in the smooth variation external conditions. So, these constructions can not be appreciated as the concretely determined result.

5 Several first droplets

The leading correction term doesn't depend on the volume of the system. It means that the deviation in the mean number of droplets from the value predicted by TAC doesn't increase with increase of the volume. The latter means that namely the first several droplets are responsible for initiation of corrections to the mean value of droplets. So, now we shall show how many droplets are responsible for these corrections.

We know that on one hand the Gaussian distribution can not be applied as statistics for the first droplets and on the other hand the big droplets are extremely important in kinetics, which lies in the base of iteration method. So, it is reasonable to use the explicit numerical simulation to see the role of several first droplets.

We start consideration of the role of several first droplets with the case of decay. Figure 4 illustrates the role of the stochastic appearance of the first droplet in nucleation kinetics. Here the relative excess of mean droplets number is shown.

There are two curves, both are functions of the volume of system V . The value of V is connected with the total number of droplets in TAC as $N_{TAC} = 1.28V$.

The broken line is the result of numerical simulation for initial problem, the smooth line is the result of solution of the following problem: The first droplet appears stochastically and later all other droplets appear with probability

$$pdx \sim I\left(\frac{dt}{dx}\right)dx$$

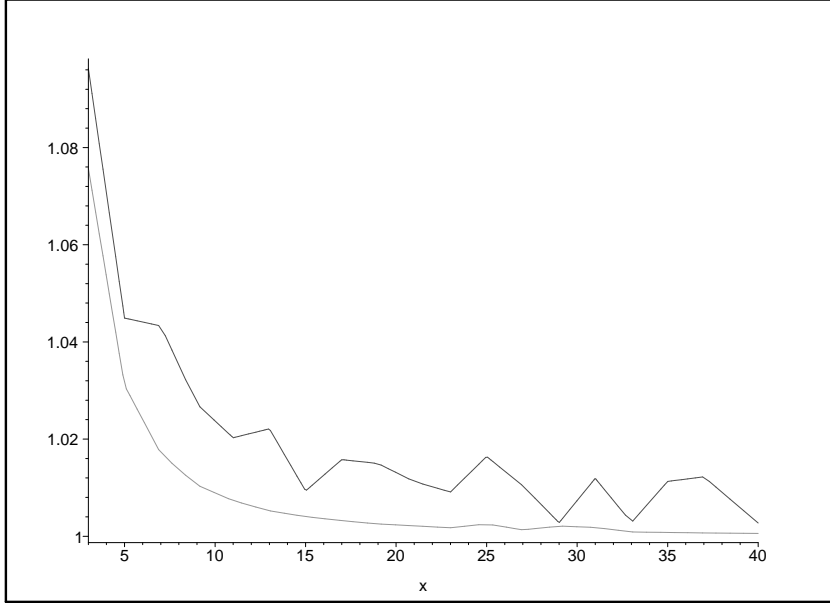


Figure 4: Relative excess of the mean droplet number. Situation of decay

Here I is the rate of nucleation. So, except the first droplet the further appearance occurs according to TAC.

One can see the satisfactory coincidence between the model and the simulation of initial problem.

One has to note that we are interested in corrections to the droplets number when they are essential. We are not interested in the tails of asymptotics.

The next picture illustrates the model with two stochastically appeared droplets. The broken line is the numerical simulation and the smooth line is the model with two stochastically appeared droplets.

Here the coincidence between the model and simulation is practically perfect. But the model with the first stochastically appeared droplet is suitable also and due to simplicity has to be considered as the basic theoretical model explaining the corrections to the mean number of droplets.

One can also investigate the model with discrete regular appearance of droplets. One can adopt that all droplets appear when

$$I_{tot} = \int_0^t I(t') dt'$$

attain integer values. In this model one can take that the first droplet appears stochastically. Nothing will be changed.

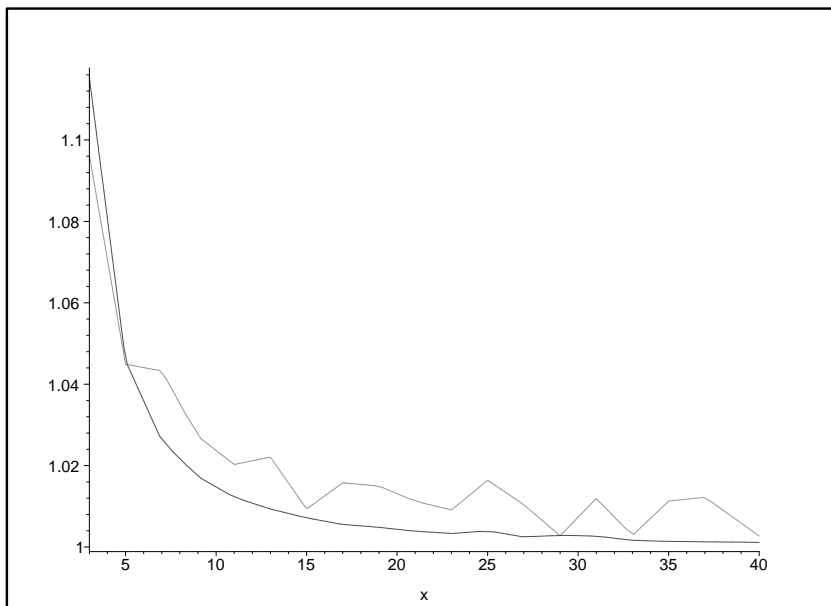


Figure 5: Relative excess of the mean droplet number. Situation of decay. The model with two stochastically appeared droplets.

The results are shown in figure 6. The axis are the same. One can see that the lower broken line which is the result of the last model has nothing in common with the upper line which is the result of simulation. So, we have to conclude that the discrete effects don't manifest themselves in nucleation kinetics.

One can observe one interesting feature of kinetics. If in the first moments of nucleation period the number of appeared droplets is higher than the average value then the total number of droplets will be lower than the average total value of the droplets number. This effect will take place at rather big value of the total number of droplets. At the small numbers of the average total number of droplets the effect will be the opposite one.

Now we shall turn to investigation of the nucleation under the smooth external conditions.

Figure 7 shows results of regular continuous solutions with several first droplets born stochastically. There are three curves drawn in this figure. The oscillating curve is numerical solution, two smooth curves are approximations with the only first droplet born stochastically and with the first two droplets born stochastically. It is clear that there is no big difference between these

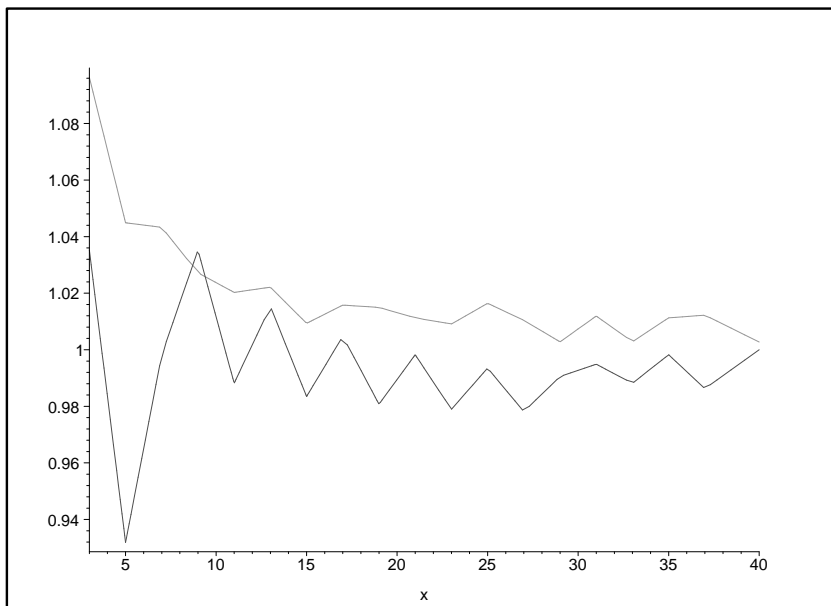


Figure 6: Relative excess of the mean droplet number. Situation of decay. The discrete model and simulation of initial problem.

curves. It means that it is sufficient to take into account only the stochastic appearance of the first droplet.

We see that the coincidence is rather satisfactory.

Now we shall see how one can incorporate the discrete effects in this situations. We propose the following model. The first droplet appears stochastically and later droplets can appear only after the elementary fixed intervals. Every interval is chosen to have the integral of the rate of nucleation over time equal to V^{-1} . The vapor is consumed by the finite (big) number of droplets born in the mentioned moments of time and growing regularly. The result at small V is shown in Figure 8.

We see that the coincidence is satisfactory. May be it is even better than the result of the regular continuous model with a first stochastically appeared droplet. In any case we see that the stochastic appearance of the first stochastically droplet diminishes the role of discrete effects.

One can see that the deviation between discrete and continuous models is not big, moreover we see that the role of discrete effects is not essential in the deviation of the average number of droplets.

In this point the nucleation under conditions of decay differs from the

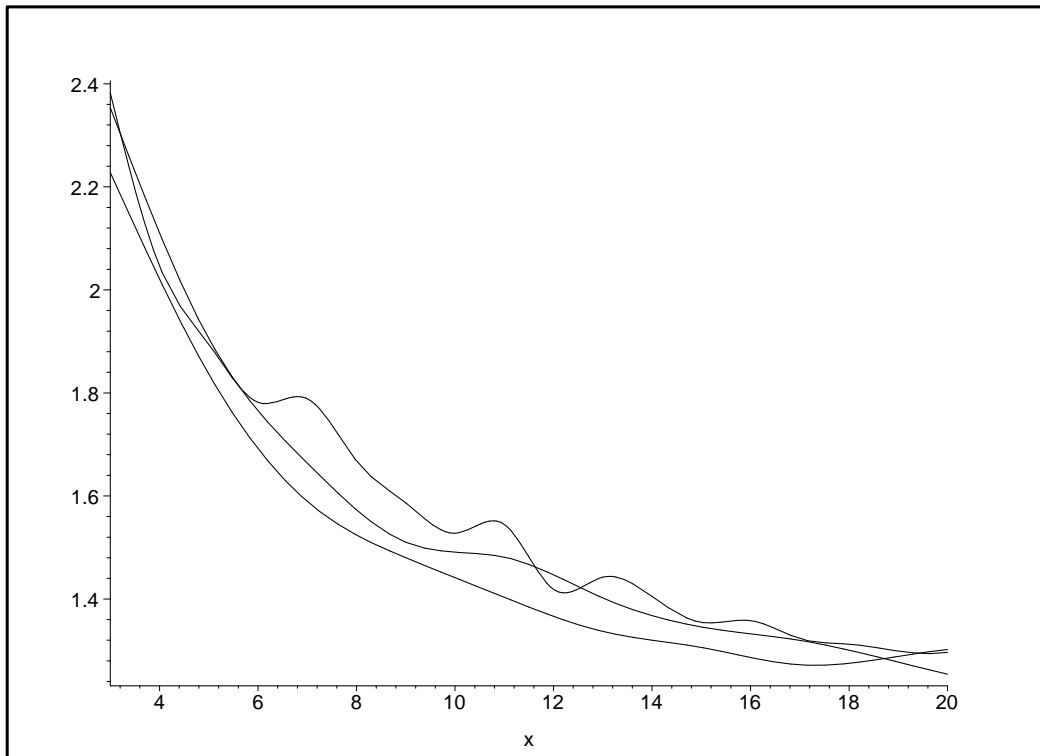


Figure 7: Numerical solution and stochastic approximations at small V . Smooth external conditions.

nucleation under the smooth behavior of external conditions.

The main result of performed simulations is that the stochastic deviation of mean value of droplets is mainly caused by the stochastic appearance of the first droplet. The stochastic appearance of the first droplet is very simple to calculate analytically. Really, we have to write the Poisson distribution for the probability of appearance of the first droplet

$$P \sim \exp(-l)$$

or more concretely for staying without appearance of any droplet. Here l is the number of possible events. Now we have to come from l to the time t . This connection is given by

$$l = \exp(t)$$

in appropriate renormalization of time t . Certainly this connection corresponds to the linearization of ideal supersaturation (see [4]) and the ideal rate

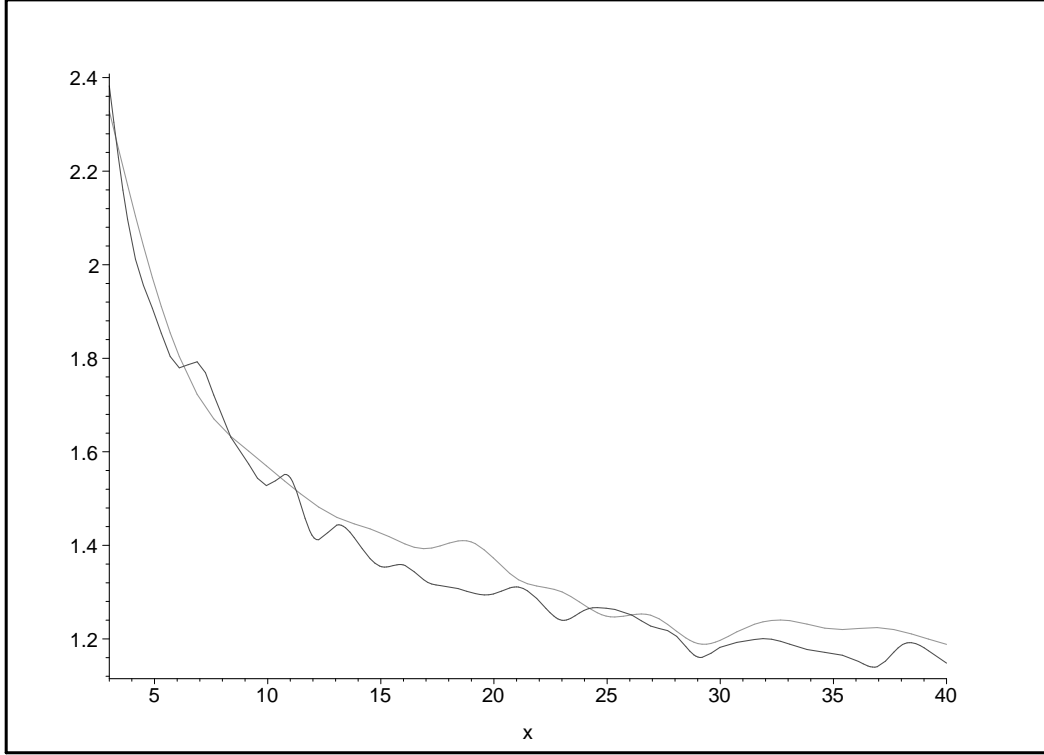


Figure 8: Numerical solution and stochastic discrete approximation at small V .

of nucleation will be like $\exp(x)$. Until the appearance of the first droplet the supersaturation is certainly the ideal one. Then it is easy to get the differential distribution p over t as

$$pdt = Pdl$$

Then

$$p = \exp(t) \exp(-l) = \exp(t - \exp(t))$$

It is remarkable that the last distribution is the same as the universal distribution of droplets in TAC established in [3].

One can write the Poisson distribution for the appearance of the first droplet $p_1 \sim l^1 \exp(-l)$, for appearance of the first two droplets $p_2 \sim l^2 \exp(-l)/2$, for appearance of n droplets $p_n \sim l^n \exp(-l)/n!$, etc. When $n \ll N_{tot}$ one can use $l = \exp(t)$ to recalculate $p(t)$ on the base of $P(l)$. This restriction isn't essential because at least $N_{eff} \ll N_{tot}$ and one needs $n < N_{eff}$.

The effects of discrete model can be also described analytically. It is simply necessary to substitute in TAC the integral by the sum. One can act in two ways.

The first possibility is to take explicitly into account several first droplets (let it be K). Then the number of droplets in a liquid phase will be

$$g = \sum_i^K (z - x_i)^3 + f_* \int_{z_c}^z (z - x)^3 \exp(x - g(x)) dz$$

where f_* is the "amplitude of spectrum" (see [2]) and $z_i \equiv x_i$ are determined by

$$f_* \int_{-\infty}^{z_i} \exp(x) dx \equiv \exp(z_i) = (i + 0.5)$$

and

$$f_* \int_{-\infty}^{z_c} \exp(x) dx \equiv \exp(z_c) = (i + 1)$$

Then the methods of solution are quite analogous to [2].

Another possibility is to use the Euler-McLorrain decomposition for

$$\sum_{i=1}^K z_i - \int_{-\infty}^{z_c} \exp(x) dx$$

This approach leads to Bernoulli numbers and will be published separately.

Also one can use discrete approximation for all droplets and replace it by the integral with the help of the global Euler-McLorrain decomposition.

6 Concluding remarks

Generally speaking the most important result of the given consideration is the zero correction in the main term of the shift of the mean droplets number. The consequence is the conclusion that only several few droplets are responsible for corrections in the mean number of droplets. The fact that only several first droplets form correction in the total number of droplets is rather important for applicability of proposed method to calculate corrections. The use of monodisperse approximation with a fixed boundary is possible only in the case when the first correction term is the zero one and the first nonzero term corresponds to the finite (independent on V) absolute shift in the number of droplets. Only then the shift is initiated by several

first droplets and there is no difference whether we take into account the rest droplets in the monodisperse peak or not. One can note that the difference between the fixed boundary and the floating boundary is reduced only into account of the rest droplets. So, there is no difference what type of boundary is used (this isn't true for other characteristics like dispersion).

Nevertheless we shall give the corresponding derivation in frames of floating boundary. This is done to show the role of non-gaussian effects (the distribution isn't the gaussian one). Having written the expression for $\langle N_{tot} \rangle$

$$\langle N_{tot} \rangle = \frac{\int_{-\infty}^{\infty} dy \int_{-3+y}^{\infty} dx \exp(x - \frac{1}{27}(x - (3+y))^3) dx P(y)}{\int_{-3+y}^{\infty} dx \exp(x - \frac{1}{27}(x - (3+y))^3) dx}$$

where y is the shift and $P(y)$ is the partial distribution over coordinate y , one can get corrections for $\langle N_{tot} \rangle$.

For the partial distribution $p(y)$ one can write

$$p(y)dy = P(N)dN$$

where $P(N)$ is the partial distribution over possible droplets N . Having written

$$dN/dy = d \exp(N)/dy = \exp(N)$$

one can get $P(N)$. For $P(N)$ one can write the ordinary gaussian distribution

$$P(N) \sim \exp(-\frac{(N - \langle N \rangle)^2}{2 \langle N \rangle})$$

After transformations we see that

$$P(N) = \exp(-\frac{(\exp(-3-y) - \exp(-3))^2}{2 \exp(-3)})$$

or

$$P(N) = \exp(-\frac{\exp(-6)(\exp(-y) - 1)^2}{2 \exp(-3)})$$

Having fulfill decompositions we get

$$P(N) = \exp(-\frac{\exp(-6)(1 - y + y^2/2 + \dots - 1)^2}{2 \exp(-3)})$$

and with restriction of first terms

$$P(N) = \exp(-\frac{\exp(-6)(y - y^2/2)^2}{2 \exp(-3)})$$

or finally

$$P(N) = \exp\left(-\frac{\exp(-6)y^2}{2\exp(-3)}\right) \exp\left(-\frac{\exp(-6)y^3}{2\exp(-3)}\right)$$

Having extracted Gaussian distribution we get

$$P(N) = \exp\left(-\frac{\exp(-6)y^2}{2\exp(-3)}\right) \left(1 - \frac{\exp(-6)y^3}{2\exp(-3)} + \dots\right)$$

So, there appear the non-gaussian corrections. Namely these corrections are the reason of appearance of corrections in the total number of droplets. They can be easily calculated by the manner described in calculations in the model with a fixed boundary.

Here we shall stop our calculations and put a question what distribution has to be a gaussian one: the distribution $P(N)$ or the distribution $P(y)$? Certainly there is no clear answer on this question. Moreover the results of [11] shows that there is a real difference when gaussian distribution instead of the Poisson distribution is used. Here it is clear that we have to use the Poisson distribution. But then to fulfill the integration one has to use the steepens descent method which is equivalent to the use of the gaussian distribution with corresponding corrections.

So we came to a paradox and it can not be resolved without taking into account that several first droplets are the reason of the shift of the mean number of droplets. Fortunately, there is no need to continue this procedure and one can take into account the influence of several first droplets explicitly by the procedure described above.

In investigation of the shift to the droplets number one has to take into account that the asymptotic we need is the "intermediate asymptotic". There is no necessity to know for example that instead of 10000 there will be 10005 droplets. We need the shift where it is at least few percent. So, we need asymptotics at the intermediate mean number of droplets. Namely this case was investigated and it was shown that already account of two or three first droplets is sufficient for the true shift of the droplets number.

We have to note that there is another reason of applicability of monodisperse approximation with a fixed boundary. This reason lies in construction of monodisperse approximation and it is different for decay and for smooth variation of external conditions. For the situation with the smooth variation of external conditions one can note that the amplitude $\exp(-3)$ corresponding to the moment of formation of monodisperse peak is very small. So, the

value $y \exp(-3)$ will be small. Then we can neglect y in the lower boundary of integration and come to the approximation with a fixed boundary instead of approximation with a floating boundary. So, the smallness of $\exp(-3)$ is the reason why one can use approximation with a fixed boundary.

In the situation of decay there is no such smallness of amplitude. But one can recall that the shift of monodisperse approximation (i.e. the position of peak formation) was chosen in such a way that "the length" of peak corresponds to the extremum of droplets number (see [9]). So, the derivative of the total number of droplets over the length of spectrum is zero and there is no difference whether to use the fixed boundary or to use the floating boundary. Here appears the physical reason of the choice of monodisperse approximation in a way prescribed in [9]. Certainly neither the approximation of fixed boundary nor approximation of floating boundary reflect the right physical evolution but such a choice of monodisperse approximation allows to ignore this problem.

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